TOC and NO3-, two natural tracers of infiltration with different hydrochemical behaviour in karst aquifers

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Abstract

Analysis of TOC and NO_3^- contents in the water at four springs in the province of Malaga (southern Spain), sampled under different hydrologic conditions, revealed two different hydrochemical behaviour patterns for these natural tracers of infiltration. TOC content increased during every recharge period, following the rapid arrival of water infiltrating through the soil. On the other hand, NO_3^- content only rose during the first flood episodes (normally in autumn), and fell during the winter and spring ones. This difference is the consequence of the distinct biogeochemical kinetics of nitrogen with respect to organic carbon, both in the soil and within the aquifer. Unlike the mineralisation undergone by TOC from the surface to the spring, the NO_3^- ion remains in the aquifer almost unaffected, due to the oxidising conditions prevailing within the karst medium, which impede its denitrification and favour its preservation within the saturated zone. TOC and NO_3^- have a common origin in the soil and can be used to determine infiltration processes and the hydrogeological functioning of karst aquifers. Their different hydrogeochemical evolution provide information about mineralization and degradation processes of organic matter within karst aquifers, which can be used to validate the vulnerability to contamination in this type of medium.

1. Introduction

In uncontaminated karstic aquifers, TOC and NO_3^- contents have a common origin in soil, with the participation of biological activity and organic matter. Both are natural tracers that provide information about hydrogeological characteristics and functioning of karst aquifers, especially regarding the participation of soil and unsaturated zone. These parameters enable us to characterise infiltration processes, water transit time and flow conditions within karst systems (Emblanch *et al.* 1998; Batiot *et al.* 2003; Perrin *et al.* 2003; Pronk *et al.* 2006). However, due to the different biogeochemical cycles presented by C and N, both in edaphic layer and within the aquifer, the information provided by these two natural tracers may not be the same.

Unsaturated zone in a karst aquifer may be considered as an open and oxidising system (Ford & Williams 2007). Under these conditions, organic carbon dissolved in water is rapidly mineralised to inorganic carbon following its entry into the system. On the contrary, NO_3^- remains almost unaltered, because reduction conditions, or at least, a certain oxygen deficit, are required for denitrification processes to take place. Accordingly, the patterns of TOC and NO_3^- evolution are different within the aquifer.

The aim of the present study is to illustrate the different hydrochemical dynamics presented by TOC and NO_3^- within karst systems, and to demonstrate the influence of the hydrogeological functioning of these aquifers on the behaviour of the above parameters. For those ends, the hydrochemical response of the water drained by four springs with a different behaviour in southern Spain (Fig. 1) was monitored and analysed.

2. Description of the test sites

Carbonate aquifers of Alta Cadena, Los Tajos and Sierra Tejeda (Fig. 1) are located approximately 30km NE and E of the city of Malaga (southern Spain). The relief is very rugged with altitudes ranging from 600 to 2050m above sea level. The predominant climate in the region is mild Mediterranean, with mean annual precipitation and temperature values of 850mm and 17°C, respectively. From a geological and hydrogeological standpoint, Alta Cadena and Los Tajos aquifers are comprised of Jurassic limestones and dolostones, with a joint thickness of 250-400m, which at the bottom present Upper Triassic clays and evaporites (gypsum) and, at the top, Lower Cretaceous-Oligocene marly limestones and marls. Sierra Tejeda aquifers is formed of Triassic calcareous and dolomitic marbles (joint thickness, 600m), with Lower Triassic-Palaeozoic metapelites as basement rocks. Recharge takes place through direct infiltration of rainwater and snowmelt, while discharge is produced through springs at the borders of the carbonate outcrops: Vva. del Rosario (755m a.s.l.) and Pita (825m a.s.l.) in Alta Cadena (Fig. 1B), Auta (620m a.s.l.) in Los Tajos (Fig. 1C), and Fájara (420m a.s.l.) in the southern sector of Sierra Tejeda (Fig. 1D). The general hydrogeological characteristics of these aquifers have been described in previous works (Pérez-ramos & Andreo 2007; Mudarra & Andreo 2011; Mudarra *et al.* 2011).

Surface karstification is not homogeneous in the study areas. At higher altitudes, karst landforms are more highly developed, especially over the limestone outcrops of Alta Cadena and Los Tajos, and above the limestone marbles of Sierra Tejeda. In these areas, epikarst is made up of karrenfield, dolines and some uvalas (Alta Cadena) with karst swallow holes, active during abundant rainfall. In all cases, epikarst features are formed within bare carbonate rock, but locally patchy soils exist up to several tens of centimetres thick, especially in dolines and beneath steep areas. Consequently, vegetation is scant and of a Mediterranean type. The study areas contain few potentially contaminant activities, limited to diffuse livestock farming activity over the carbonate outcrops and concentrated in shallow-sloping or karst depressions, exceptionally, in the vicinity of some springs.

3. Methodology

Between September, 2006 and April, 2009, discharge, electrical conductivity (EC) and water temperature, together with TOC and NO_3^- contents, were monitored in water from the four springs examined in this study, generally at weekly intervals, but daily during some high water periods and fortnightly during depletion periods. The total number of samples obtained (421) was not the same at all points (Table 1). Water temperature and EC were measured in situ usually using portable equipment (discontinuous records) and datalogger devices (continuous records) with a precision of ±0.1ºC and ±1µS/cm respectively. NO_3^- content was analysed at the Centre of Hydrogeology of University of Malaga using ion chromatography (Metrohm, 791 Basic IC model), with a precision of ±0.01mg/L. TOC content

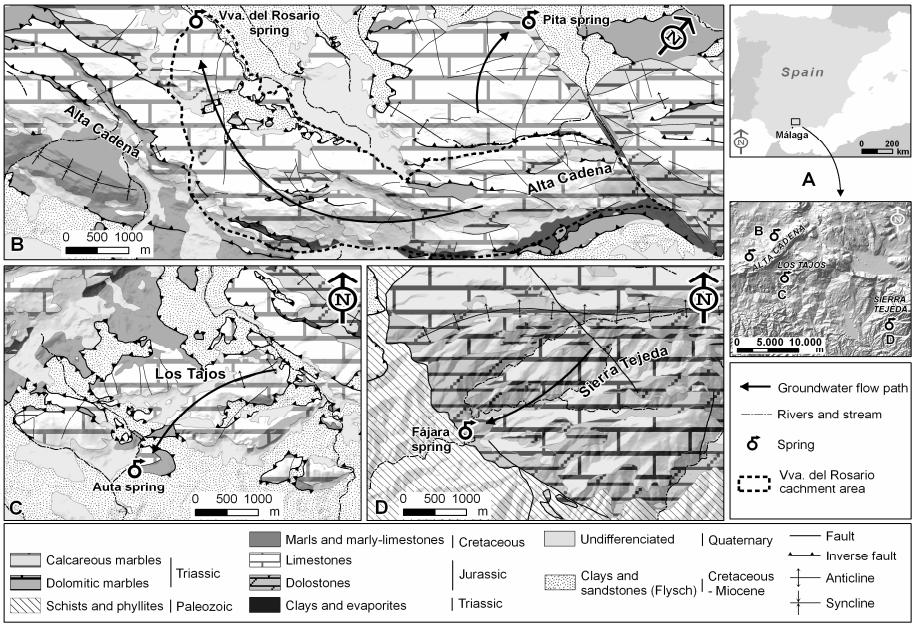

Fig. 1
Location (A) and hydrogeological sketchs of the four test sites.

was measured by combustion of the organic matter present in the samples using a Shimadzu V-TOC carbon analyser, calculated as total carbon less inorganic carbon.

4. Results

The highest mean values for EC and water temperature were recorded in Auta spring (616µS/cm and 16.9ºC, respectively), while the lowest mean values corresponded to Pita spring (246µS/cm and 12.9ºC) (Table 1). Mean NO_3^- values ranging from 2.8mg/L (Fájara) to 11.2mg/L (Auta). In general, the spring water had a low–very low TOC content, with mean values ranging from 0.25mg/L (Pita) to 0.41mg/L (Auta). Fájara spring, with 223L/s, presented the highest mean discharge value, followed by Vva. del Rosario (192L/s) and Auta (128L/s. Pita spring had the lowest mean outflow (35L/s).

Variations in discharge and response time to precipitation events differed from one spring to another (Fig. 2). Thus, Vva. del Rosario and Fájara springs recorded sharp rises in outflow, from 7 to 2445L/s and from 2 to 1860L/s, respectively, during the recharge periods (Figs. 2A, 2D), with similar reductions when rainfall ceased. The spring at Auta presented outflow variations from 11 to 1050L/s (Fig. 2C). Finally, Pita spring presented the smallest discharge variations, from 7 to 219L/s (Fig. 2B) and also the longest response times following rainfall events.

Each spring presented a different hydrochemical response to precipitation, both for mineralisation (EC) and for natural tracers of infiltration. Thus, in Vva. del Rosario spring water (Fig. 2A), the highest EC values were recorded during summer and early autumn, while rapid, sharp reductions of up to 150µS/cm followed each recharge event. A similar behaviour pattern was found at Fájara spring, where significant rainfall events provoked a rapid fall in EC (Fig. 2D), from values close to 350µS/cm to less than 250µS/cm. At Auta spring, the general evolution of EC was similar to that at the above two springs, although somewhat buffered (Fig. 2C). Thus, during the summer months, EC progressively rose until, with the autumn rainfall, a slow, slight fall took place (from 625 to 575µS/cm), within a general falling trend during the autumn and winter periods. Finally, Pita spring responded relatively rapidly to rainfall events, but, unlike at other three springs, recharge periods produced an increase in EC, of up to 65µS/cm (Fig. 2B).

	Spring	Discharge (L/s)	E.C. (µS/cm)	T (ºC)	TOC (mg/l)	NO_3 (mg/l)
n	Vva. Del Rosario	912	119	118	109	109
min		7	247	12,6	0,16	1,7
max		2445	457	14,3	0,75	9,0
m		192	358	13,4	0,26	5,4
CV (%)		135,3	12,3	2,8	38,2	25,7
n	Pita	102	112	112	96	96
min		7	234	12,6	0,00	4,2
max		219	303	13,3	0,76	10,2
m		35	246	12,9	0,25	7,0
CV (%)		119,2	5,7	1,1	50,2	14,2
n	Auta	105	124	120	125	125
min		11	574	16,6	0,19	6,4
max		1050	651	17,1	1,12	14,4
m		128	616	16,9	0,41	11,2
CV (%)		145,8	3,3	0,5	38,3	15,7
n	Fájara	92	92	92	91	91
min		2	253	13,1	0,06	1,0
max		1860	389	16,7	0,86	5,1
m		223	313	14,8	0,27	2,8
CV (%)		154,0	8,2	5,7	53,2	30,3

Table. 1 Statistical parameters of the water samples analysed from the 4 springs during the study period. (n) number of samples, (m) mean, (CV) coefficient of variation, (EC) electrical conductivity, (T) temperature.

The hydrothermal response in water from Fájara and Vva. del Rosario springs shows significant decreases in temperature during recharge events, (up to 2.5°C at Fájara) followed by rapid, progressive increases of a similar magnitude. The highest temperatures were recorded in late summer and early autumn, while the lowest ones corresponded to winter and spring months. The range of variation of water temperature at these springs was 3.6°C and 1.7°C, respectively. Water temperature at Pita had a smaller range of variation (0.8°C) and the seasonal variation was mainly influenced by air temperature variations, with recharge having little or no influence on water temperature. Finally, water from Auta spring presented the lowest hydrothermal variations in response to precipitation events during the study period (0.5°C).

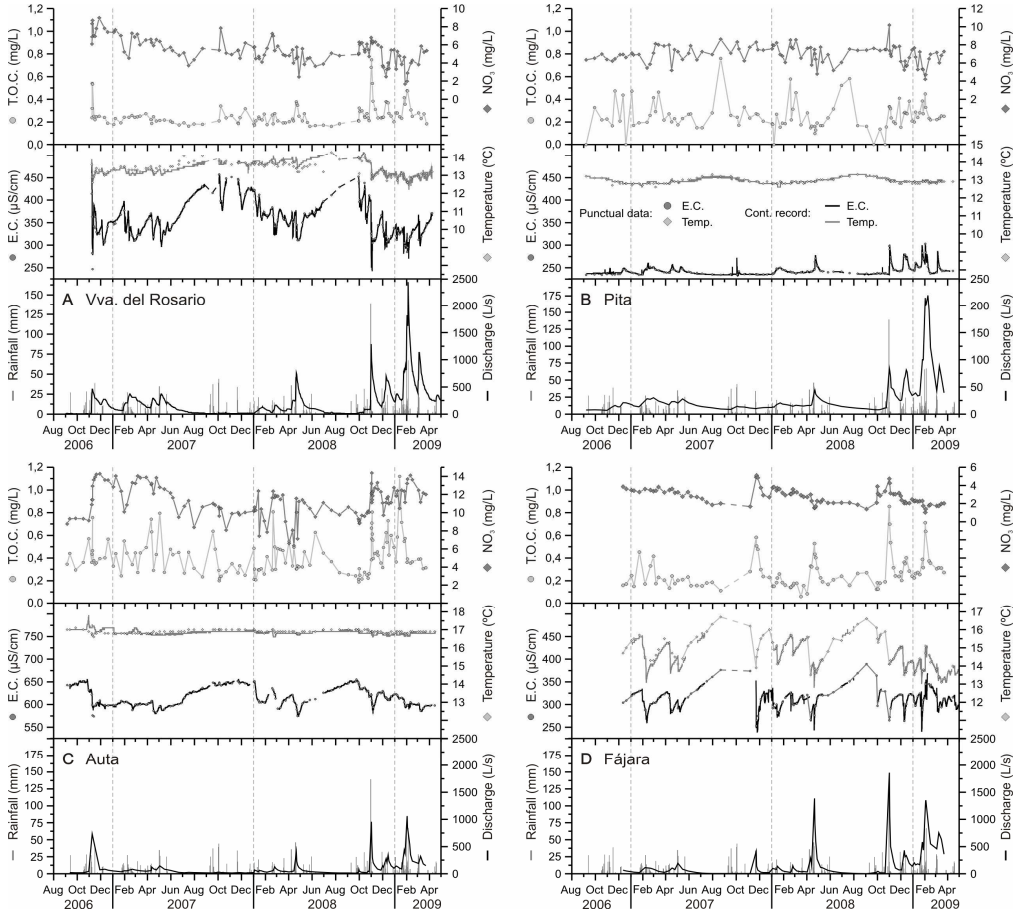

Fig. 2 : Evolution of discharge rates, electrical conductivity, water and natural tracers (TOC and NO_3^-) of the water from the springs.

With respect to NO_3^- content, each spring presented a different temporal evolution, although with a similar hydrochemical behaviour, which was particularly well defined at the water from Fájara spring, and characterised as presenting a falling trend during the hydrological year. NO_3^- content tends to be higher at the beginning of the hydrological year (autumn), when the first recharge events take place, and falls as the springs move into low-water conditions. During the subsequent winter and spring recharge periods, NO_3^- concentrations fall at all springs, in proportion to the magnitude of precipitation. The increases recorded may be single-occurrence, if an important magnitude rainfall occurs in autumn (for example, at Fájara, in autumn 2007), or they may present various peaks, if before the more abundant precipitation events other, less significant ones take place (Vva. del Rosario and Fájara, in autumn 2008). Moreover, these increases may occur gradually (Auta in autumn 2006, 21 days to the maximum value) or be immediate (Pita, in autumn 2008, one day). In some cases (Vva. del Rosario, autumn 2006; Auta, autumn 2008), a single recharge event may give rise to two peak values for NO_3^- concentration: the first of these, more rapid and accentuated, coincides with the increased outflow from the spring, while the second, more buffered, takes place during recession period.

TOC content in spring water increased during the main recharge periods, followed by decreases of a similar magnitude. During summer of 2007 and, above all, during the summer months of 2008, there was a gradual increase and subsequent decrease in TOC at Pita and Auta springs (Figs. 2B, 2C), which was not caused by precipitation events. Unlike the case of NO_3^- content, TOC content increased were always punctual and rapid, and also proportional to the intensity and magnitude of precipitation events. However, on some occasions (Auta, autumn 2008), a single pluviometric event could give rise to two TOC spikes, as occurred with NO_3^-: the first of these was more rapid and accentuated, and coincided with increased outflow from the spring, while the second was more buffered and longer lasting, and took place during falling outflow.

5. Discussion

The spring waters examined in this study had very low TOC content (Tab. 1), in comparison with other karst systems (Emblanch *et al.* 1998; Batiot *et al.* 2003; Perrin *et al.* 2003; Pronk *et al.* 2006). This is mainly due to the poor development of the soil, and therefore of vegetation, with subsequent low content of organic matter. Nevertheless, in Auta spring water maximum TOC concentrations of 1.12mg/L were recorded (Table 1). With respect to NO_3^- content, these are similar in all cases (almost always below 9mg/L, Table 1), although again Auta spring presents higher mean values (11.2mg/L). This seems to indicate the existence of an incipient degree of contamination in the aquifer, apart from natural NO_3^- enrichment processes in soil. In fact, mean NO_3^- content in rainwater between September, 2006 and April, 2009 was 1.9mg/L (72 samples).

The springs present differing patterns of hydrogeological behaviour, with different hydrodynamical, hydrochemical and hydrothermal responses to recharge

events (Fig. 2). Thus, Vva. del Rosario and Fájara present the largest and most rapid variations in discharge, EC and water temperature in response to recharge events (Figs. 2A, 2D). This reveals the existence of rapid flows of infiltration water from aquifer surface to springs, via karst conduits. On the contrary, the variations recorded in the water from Pita and Auta are much more buffered and occur with some delay following precipitation (Figs. 2B, 2C). This suggests a slower flow, which is typical of aquifers with a lower degree of karstification. The EC increased recorded at Pita spring during recharge events is caused by a piston effect in the unsaturated zone (Mudarra & Andreo 2011).

With respect to the content of TOC and NO_3^-, which are natural tracers of infiltration (Batiot *et al.* 2003; Perrin *et al.* 2003), spring waters present two different behaviour patterns. TOC content increases during recharge periods, as a consequence of the rapid arrival at springs of water infiltrating through the soil. This increase is greater, more marked and more rapid at Vva. del Rosario and Fájara springs than at Auta and Pita (Fig. 2), which drain systems with a lower degree of functional karstification. On the other hand, the NO_3^- content presents a generally falling trend throughout the hydrological year, this being particularly visible at Fájara spring. Increases in NO_3^- content take place only at the beginning of the hydrological year, with the autumn flooding, and the value falls during the winter and spring.

High concentrations of TOC and NO_3^- detected at the beginning of the hydrological year are due to the leaching of the soil, which has been subjected to biological activity, in the absence of rainfall, since the end of previous spring time. For this reason, the infiltration water associated with the first autumn rainfall normally has a higher content of these components, which decreases when hydrological year advances and discharge from the spring declines. Nevertheless, in some cases there are increasing contents of NO_3^-, but not of TOC (Fájara, autumn 2008), or vice versa (Auta, autumn, 2008) (Figs. 2D, 2C). The different behaviour patterns presented by TOC and NO_3^- are result of the differing biogeochemical kinetics of nitrogen with respect to organic carbon, both in the soil and within the aquifer (Toran & White 2005; Sánchez-monedero *et al.* 2001). Unlike the mineralisation and transformation into TAC that is undergone by the TOC in its flow from the surface to the spring, NO_3^- ion remains in the aquifer almost unaffected, due to the oxidising conditions prevailing in the karstic medium and to the short transit time of water from surface to springs. These factors impede its denitrification and favour its preservation in flow through the unsaturated and the saturated zones. Hence, successive winter recharges, such as those described in this study, do not mobilise significant quantities of NO_3^- from the soil, but dilute its content in the aquifer water, together with other parameters of water mineralisation. The duality of the hydrochemical behaviour of TOC and NO_3^- is more evident with higher development of functional karstification, although this feature may be modified by contamination processes, as observed at Auta spring.

6. Conclusions

Monitoring and analysis of the TOC and NO_3^- content of the water drained by four springs in southern Spain reveal the differing hydrochemical behaviour of these two natural tracers of infiltration in karst aquifers. This is a consequence of the different biogeochemical kinetics of nitrogen respect to organic carbon, both in the soil and within the aquifer, but also of the water flow characteristics and, ultimately, the degree of karstification within the aquifer. Thus, this study shows that as more intense karst functioning of the system, better defined is the hydrochemical behaviour of TOC and NO_3^- in the water and, therefore, greater differences exists between its natural responses. Nevertheless, the presence of contamination, albeit slight, can modify these patterns. The results presented enable us to better understand processes of mineralisation and degradation of organic matter within karstic aquifers, as well as the hydrogeological functioning and vulnerability to contamination of this type of medium. In futures studies it would be analysed the input functions of NO_3^- and TOC in karst aquifers.

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